reduced pressure. White crystals were separated, mp 84–85°, and identified by mixture melting point as the starting material.

Basic Hydrolysis of 3,3-Di-*tert*-butyl Diperoxyphthalide.—3,3-Di-*tert*-butyl diperoxyphthalide (0.10 g, 0.3 mol) was dissolved in 6 ml of ethylene glycol monomethyl ether and to the solution was added 0.8 ml of 10% aqueous sodium hydroxide. The reaction mixture was stirred for 2 hr at 40°; then, added to it successively were 15 ml of acetic acid, 3 ml of saturated potassium iodide solution, and a piece of Dry Ice. After standing for 0.5 hr at 60°, the iodine liberated was titrated with standard sodium thiosulfate. On the basis of formula III, 86.5% of the expected 2-mol equiv of *tert*-butyl hydroperoxide was found. In a separate experiment one of the hydrolysis products, phthalic acid, was isolated by extracting the acidified reaction mixture with ether and evaporating the solvent. A white solid was obtained, mp 186–187°, and identified as phthalic acid by mixture melting point.

Registry No.—I, 15042-77-0; II, 2155-71-7; III, 15044-23-2; *sym*-phthaloyl chloride, 88-95-9; *unsym*-phthaloyl chloride, 30247-86-0; *tert*-butyl hydroperoxide, 75-91-2.

Acknowledgment.—The authors wish to thank Dr. Nagy for the combustion analyses, the Lucidol Division of Wallace and Tiernan, Inc., and the Industrial Fund of Massachusetts Institute of Technology for financial support of this investigation.

Synthesis of Methyl 14-Methyl-*cis*-8-hexadecenoate and 14-Methyl-*cis*-8-hexadecen-1-ol. Sex Attractant of *Trogoderma inclusum LeConte*

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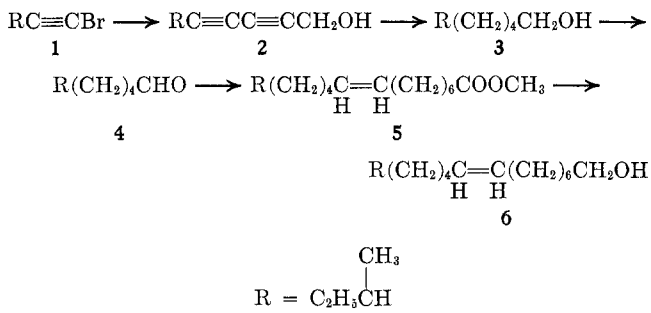
The title compounds have been previously identified[1] as components of the sex attractant of *Trogoderma inclusum LeConte*. Evidence has also been obtained that other *Trogoderma* species respond to these attractant compounds. Although the structures are relatively simple, their synthesis in acceptable yields is complicated by the unavailability of suitable starting materials for the branched portion of the chain. A convenient synthesis of the compounds is the subject of this communication.

Preparation of the key reagent, 6-methyloctanal (**4**), initiated with 3-methyl-1-pentyne which was brominated (NaOBr) to give the 1-bromoalkyne (**1**) in 80% yield. Coupling with propargyl alcohol afforded in 69% yield the diynol **2**, which was easily hydrogenated to yield 6-methyloctan-1-ol (**3**). An alternate synthesis[2] of **3** from 4-oxo-6-methyloctanoic acid was impractical because of the difficulty in obtaining complete reduction of the keto group.

Several of the methods reported in recent years for the oxidation of primary alcohols to aldehydes were investigated for the conversion of **3** to the aldehyde **4**. None were found to be acceptable; however, we were able to obtain **4** in good yield by a modification of the chromic acid–pyridine reagent. The yellow, solid complex was prepared in pyridine[3] and the excess pyridine was removed with hexane. The isolated solid was immediately dissolved in CH_2Cl_2 followed by addition of the alcohol. Yields of 60–70% of distilled aldehyde **4** were realized when a ratio of 6:1 of reagent to



alcohol was employed. We have found the procedure to be quite reliable for the preparation of other, more complex aldehydes. A recently reported[4] variation of the related Collins reagent[5] appears to be equally effective and has an advantage in convenience.

The remainder of the carbon chain was inserted *via* the Wittig condensation of 6-methyloctanal (**4**) with the triphenylphosphinylide of methyl 8-bromooctanoate. When conducted in DMF solution[6] the olefinic ester product **5** was contaminated by only 5–10% undesired trans isomer. Reduction of the ester with $LiAlH_4$ in ether afforded the alcohol **6**.

Experimental Section

1-Bromo-3-methyl-1-pentyne (**1**).—To a solution of 8.9 g of sodium hydroxide in 23 ml of water and 45 g of ice was added 4.9 ml of bromine over 5 min. The hypobromite solution, at 0–5°, was then added rapidly to 7.3 g of 3-methyl-1-pentyne, followed by the addition of 12 ml of pyridine. The mixture was stirred for 16 hr and extracted with 100- and 50-ml portions of ether. The ether was washed with 100 ml of water, 90 ml of 2 *N* HCl, 50 ml of water, and 30 ml of saturated sodium bicarbonate. After drying over magnesium sulfate the solvent was distilled off through a Vigreux head to leave 11.5 g (80%) of pale yellow liquid. A sample was distilled for analysis, bp 35–36° (24 mm).

Anal. Calcd for C_6H_9Br: C, 44.8; H, 5.63. Found: C, 44.8; H, 5.61.

6-Methyl-2,4-octadiyn-1-ol (**2**).—To an ice-cold mixture of 24.3 ml of 33% ethyl amine, 0.21 g of cuprous chloride, 0.43 g of hydroxylamine hydrochloride and 4.0 g (0.071 mol) of propargyl alcohol was added, dropwise with stirring, 11.5 g (0.071 mol) of crude bromopentyne (**1**). The yellow mixture was stirred for 16 hr at ambient temperature, becoming a blue-green color. After treatment with 0.75 g of potassium cyanide the now orange mixture was diluted with 150 ml of water and extracted twice with 60-ml portions of pentane. The pentane was washed with water (50 ml), dried over magnesium sulfate, and evaporated to leave 7.3 g of amber liquid. The material was distilled to afford 6.6 g (69%), bp 74–75° (1.25 mm), ir (film) intense 4.45 μ (conjugated diyne).

Anal. Calcd for $C_9H_{12}O$: C, 79.4; H, 8.88. Found: C, 79.4; H, 9.00.

6-Methyl-1-octanol (**3**).—A mixture of 1.00 g of diynol **2**, 100 mg of platinum oxide, and 10 ml of ethanol was stirred under 1 atm of hydrogen for 18 hr. The theoretical amount of gas was consumed. The catalyst was removed and the solvent was evaporated *in vacuo* to leave 1.00 g of a clear liquid. The infrared

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spectrum was identical with that of material prepared by lithium aluminum hydride reduction of methyl 6-methyloctanoate.[2]

6-Methyl-1-octanal (4).—To 450 ml of pyridine was slowly added 45 g of chromic acid with stirring and maintainence of the temperature below 30°. The resulting yellow precipitate was treated with 1 l. of hexane and quickly filtered. The solid was washed with hexane and rapidly dissolved in 900 ml of dichloromethane. 6-Methyloctanol (3) (9 g) was added slowly with stirring and after 10 min the supernatant was decanted from the black, gummy precipitate. The solution was washed with 300 ml of water and 450 ml of 1 *N* HCl and dried ($MgSO_4$). After evaporation of solvent the dark residue was extracted with 100 ml of hexane. The clear solution was evaporated to leave 8.5 g of colorless liquid, which was distilled to yield 6.2 g (69%) of aldehyde, bp 64–66° (6 mm), 2,4-dinitrophenylhydrazone mp 80–82° (*n*-C_3H_7OH).

Anal. Calcd for $C_{15}H_{22}N_4O_4$: C, 55.9; H, 6.88; N, 17.4. Found: C, 55.8; H, 7.01; N, 17.2.

Methyl 14-Methyl-*cis*-8-hexadecenoate (5).—A mixture of 25.0 g of triphenylphosphine, 19.0 g of methyl 8-bromooctanoate, and 250 ml of toluene was refluxed for 24 hr. The cooled supernatant was decanted and the viscous residue was dried to leave 29 g (71%) of the triphenylphosphonium salt. The crude salt (0.058 mol) in 45 ml of dimethylformamide was rapidly added to a suspension of 2.5 g (0.046 mol) of sodium methylate in 50 ml of DMF under nitrogen. After being stirred for 1 hr the yellow mixture was cooled in ice and 5.2 g (0.036 mol) of 6-methyloctanal in 25 ml of DMF was added over 10 min. The mixture was stirred for 18 hr under nitrogen and then chilled and diluted with 400 ml of water. Extraction with 100-ml and two 50-ml portions of hexane was followed by washing with 100 ml of water, drying over magnesium sulfate, and evaporation to leave 7.9 g of yellow liquid.

The crude material was saponified with 2.5 g of potassium hydroxide in 50 ml of 90% methanol to yield 2.80 g of carboxylic acid. Reesterification (methanol–toluenesulfonic acid) gave 2.64 g of ester which was chromatographed on 130 g of silica gel to afford 1.05 g of ester after elution by a 10% ether–90% benzene mixture. Glc (Carbowax 20M) showed the material to be about 90% pure when compared with the natural compound. Infrared spectra were likewise identical except for weak trans C=C at 10.3 μ.

14-Methyl-*cis*-8-hexadecenol (6).—A mixture of 0.75 g of methyl ester 5, 0.30 g of lithium aluminum hydride, and 15 ml of ether was stirred for 20 hr. The mixture was cooled in ice and excess hydride was decomposed with ethanol and water. The white, pasty precipitate was extracted with several portions of ether which were dried over magnesium sulfate and evaporated to leave 0.48 g. Extraction with pentane gave only 0.36 g of soluble material, approximately 90% pure by glc (Carbowax 20M). Further purification was carried out with preparative glc to afford material identical with the natural alcohol with regard to glc retention time, infrared spectrum, and biological activity.

Registry No.—1, 30689-73-7; 2, 30689-74-8; 4, 30689-75-9; 4 2,4-DNP, 30689-76-0; 5, 30689-77-1; 6, 30689-78-2.

Acknowledgment.—The bioassay was conducted by Dr. W. E. Burkholder, University of Wisconsin, USDA Laboratories.

Isolation of Betamethasone 17,21-Orthobenzoate

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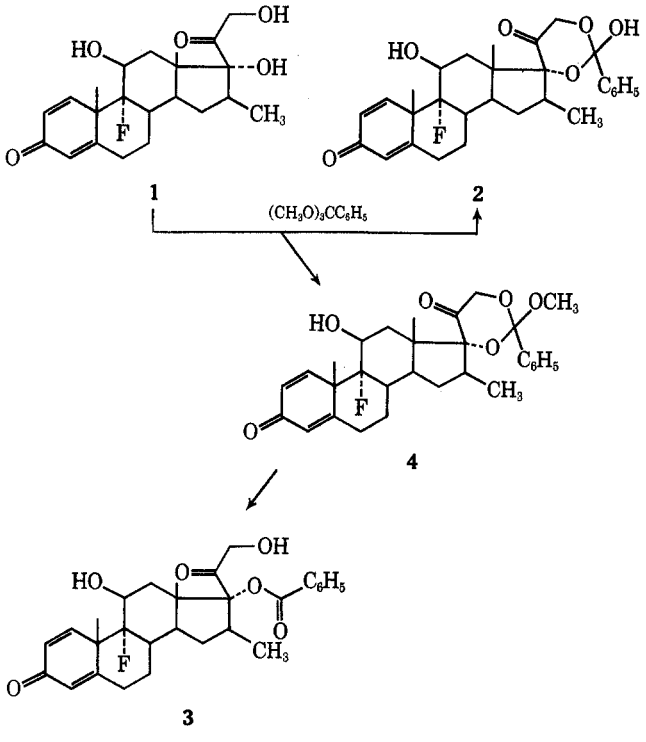
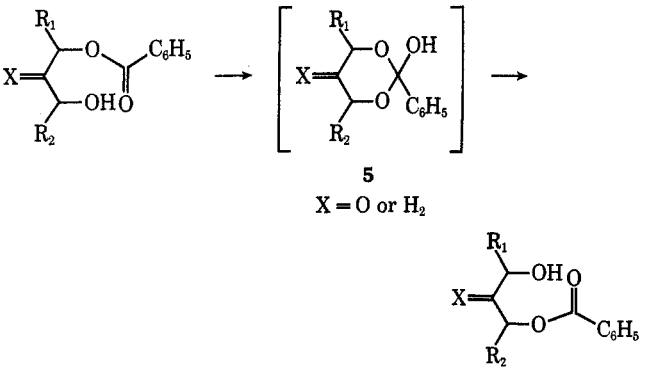
The preparation of betamethasone 17-benzoate (9α-fluoro-11β,17α,21-trihydroxy-16β-methylpregna-1,4-diene-3,20-dione 17-benzoate) (3) labeled with tritium was required in order to determine its excretion pattern and to elucidate its metabolite(s) in various animal species and man. The synthesis of the radioactive drug is reported elsewhere.[2] During the preliminary work with nonradioactive compounds, on the same small scale required for the radioactive synthesis, an unknown was isolated which possessed an unusual structure.

SCHEME I



This synthesis, as shown in Scheme I, necessitated the preparation of betamethasone 17,21-(methyl orthobenzoate) (4). This reaction produced, in addition to 4, about an equal weight of a more polar compound. The structure of this compound was shown to be betamethasone 17,21-orthobenzoate (2). Compound 2 is novel because it contains the ortho ester structure of the normally unstable intermediate 5 in the generalized migration depicted in Scheme II.

SCHEME II



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(2) E. J. Merrill and G. G. Vernice, *J. Label. Compounds*, in press.